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533 Rec'd PCT/PTO 11 SEP 2001

FORM PTO-1390 (REV. 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
0020-4902P	
U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	
09/936495 NEW	

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP00/01453	March 10, 2000	March 11, 1999

TITLE OF INVENTION

FLUORINATED ALLYL ETHER POLYMER

APPLICANT(S) FOR DO/EO/US

MORITA, Shigeru; SAKASHITA, Hirotoshi; ARAKI, Takayuki; SHIMIZU, Tetsuo

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau. WO 00/53647
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is transmitted herewith.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☒ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with cited 5document(s).
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
    Article 34 substitute claims letter

JC05 Rec'd PCT/PTO 11 SEP 2001

U.S. APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/936495	PCT/JP00/01453	0020-4902P

	CALCULATIONS	PTO USE ONLY
21. ☒ The following fees are submitted:		
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. **$1,000.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. **$710.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4). **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0.00	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	8 - 20 =	0	X **$18.00**	$ 0.00	
Independent Claims	3 - 3 =	0	X **$80.00**	$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)		Yes	+ **$270.00**	$ 270.00	
			TOTAL OF ABOVE CALCULATIONS =	$ 1130.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by I/2.				$ 0.00	
			SUBTOTAL =	$ 1130.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐20 ☐30 months from the earliest claimed priority date (37 CFR 1.492(f)).			+	$ 0.00	
			TOTAL NATIONAL FEE =	$ 1130.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00	
			TOTAL FEES ENCLOSED =	$ 1170.00	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of $ **1170.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account. No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-2448.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:
Birch, Stewart, Kolasch & Birch, LLP or Customer No. 2292
P.O. Box 747
Falls Church, VA 22040-0747
(703)205-8000

Date: September 11, 2001

By _____ #36,623
Andrew D. Meikle, #32,868

/rem

PATENT
0020-4902P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: MORITA, Shigeru et al. Conf.:

Int'l. Appl. No.: PCT/JP00/01453

Appl. No.: NEW Group:

Filed: September 11, 2001 Examiner:

For: FLUORINATED ALLYL ETHER POLYMER

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION
Assistant Commissioner for Patents September 11, 2001
Washington, DC 20231

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

After line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/01453 which has an International filing date of March 10, 2000, which designated the United States of America and was not published in English.--

IN THE CLAIMS:

Please amend the claims as follows:

4. (Amended) The fluorine-containing allyl ether polymer according to claim 1, or 7, wherein at least one of the repeating units is repeating unit of the formula:

REMARKS

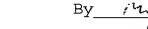
The specification has been amended to provide a cross-reference to the previously filed International Application. The claims have also been amended to delete improper multiple dependencies.

Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By  #36,623

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0020-4902P

Attachment: VERSION WITH MARKINGS TO SHOW CHANGES MADE

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE CLAIMS:

The claims have been amended as follows:

4. (Amended) The fluorine-containing allyl ether polymer according to [claim 1, 3 or 7] claim 1, or 7, wherein at least one of the repeating units is repeating unit of the formula:

DESCRIPTION

FLUORINATED ALLYL ETHER POLYMER

FIELD OF THE INVENTION

The present invention relates to a fluorinated allyl ether polymer, in particular, a homo- or copolymer of 1,1,2-trifluoroallyl ether.

BACKGROUND ART

Hitherto, it is believed that hydrocarbon allyl compounds are hardly radically homopolymerized, and no homopolymer thereof having a high molecular weight can be obtained, and the reported molecular weight of the homopolymer is from about 300 to about 3,000 (see R. L. Shriner, L. Kelley ed. "Chemical Reviews" (USA), page 815, received by the National Diet Library (Japan) on December 13, 1962).

Thus, various improvements have been made on comonomers copolymerizable with the allyl compounds. However, no publications other than the above reference has reported the homo- and copolymerization of the allyl compounds.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a polymer of a fluorinated allyl ether having a high molecular weight, which is prepared by radial homopolymerization.

This object is achieved by a fluorinated allyl ether polymer having a number average molecular weight of 1,000 to 1,000,000 and consisting of chains of at least one repeating unit of the formula:

$$-(CH_2-CF)-$$
$$\quad\quad|$$
$$\quad CF_2-O-A \qquad (1)$$

wherein A is an organic group having 1 to 100 carbon atoms, and a fluorinated allyl ether polymer having a number average molecular weight of 1,000 to 1,000,000 and represented by the formula:

$$CH_2=CFCF_2O-(CF_2O)_x-(CF_2CF_2O)_y-(CX^1_2CF_2CF_2O)_z-(CFX^2CF_2O)_w-CFX^3-R \qquad (4)$$

wherein X^1 is a hydrogen atom, a fluorine atom or a chlorine atom, X^2 is a hydrogen atom, a chlorine atom, a methyl group or a trifluoromethyl group, X^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, x, y, z and w are the same or different and a number of 0 to 20 provided that the sum of x, y, z and w is from 1 to 20, and R is -COOH, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CH_2OH$, $-CONH_2$, $-CF=CF_2$, a hydrocarbon group having 1 to 20 carbon atoms or a perfluoroalkyl group having 1 to 20 carbon atoms.

The present invention is based on the finding that the specific allyl ether structure has good homopolymerizability and provides a polymer having a high molecular weight. That is, a fluorine-containing allyl ether compound of the formula:

$$CH_2=CFCF_2-O-A \qquad (1a)$$

wherein A is an organic group having 1 to 100 carbon atoms has good homopolymerizability, in particular radical polymerizability, of the monomer of the formula (1a) due to the structure of the group: $CH_2=CFCF_2-O-$ in the formula (1a), and provides a high molecular weight polymer. This is particularly different from other allyl compounds such as $CF_2=CFCF_2OR$, $CF_2=CFCF_2R$, etc. or vinyl ether compounds such as $CF_2=CFOR$,

CH_2=CHOR, etc., which cannot be homopolymerized or which provide only low molecular weight products (oligomers), if they can be polymerized.

According to the present invention, insofar as the monomer has the group of the formula: $CH_2=CFCF_2-O-$, it can be radically polymerized irrespective of the kind of the group A, and the polymer of the formula (1) can be obtained.

DETAILED DESCRIPTION OF THE INVENTION

The fluorinated allyl ether polymer of the present invention consists of the chains of the repeating unit of the formula (1), and includes, for example, a copolymer of the formula:

$$-(CH_2-\underset{\displaystyle CF_2-O-A'}{\underset{|}{CF}})_a-(CH_2-\underset{\displaystyle CF_2-O-A''}{\underset{|}{CF}})_b-(CH_2-\underset{\displaystyle CF_2-O-A'''}{\underset{|}{CF}})_c-$$

In this formula, the order of the repeating units may be random or block.

The above polymer may be compolymerized with less than 20 % by mole, preferably less than 10 % by mole of an ethylenically unsaturated compound copolymerizable with the above fluorinated allyl ether such as a fluorine-containing olefin.

The group A may be selected from any organic groups. In general, examples of the organic group include saturated or unsaturated aliphatic hydrocarbon groups having 1 to 50 carbon atoms, aromatic hydrocarbon groups having 4 to 30 carbon atoms, etc. At least one of hydrogen atoms of these hydrocarbon groups may be substituted with a fluorine atom.

Specific examples of the hydrocarbon groups include alkyl or fluoroalkyl groups having 1 to 50 carbon atoms, alkenyl or fluoroalkenyl groups having 2 to 50 carbon atoms, alkynyl or

fluoroalkynyl groups having 2 to 50 carbon atoms, alkyl or fluoroakyl groups having an ether bond and 1 to 60 carbon atoms, alkenyl or fluoroalkenyl groups having an ether bond and 2 to 60 carbon atoms, alkynyl or fluoroalkynyl groups having an ether bond and 2 to 60 carbon atoms, aryl or fluoroaryl groups having 4 to 30 carbon atoms, etc.

The hydrocarbon group may have a functional group. When the hydrocarbon group having the functional group is used, various functions are preferably imparted to the fluorinated allyl ether polymer obtained. A specific example of the repeating unit comprising the group A having the functional group is a repeating unit of the formula:

$$-(CH_2-CF)- \quad (2)$$
$$\quad\quad\quad |$$
$$\quad\quad CF_2-O-A^1-Y^1$$

wherein A^1 is a divalent organic group having 1 to 60 carbon atoms, and Y^1 is $-CH_2OH$, $-COOH$, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CON<^{R^2}_{R^3}$ in which R^2 and R^3 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, or $-OCO-CZ^3=CZ^1Z^2$ in which Z^1 and Z^2 are the same or different and a hydrogen atom or a fluorine atom, and Z^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group.

Besides the group $-A^1-Y^1$, examples of the group A having the functional group include an epoxy group, a glycidyl group, a cyano group (-CN), a sulfonic acid group ($-SO_3H$), $-SO_3R'$ in which R' is a monovalent organic group, etc.

The group A^1 in the formula (2) may be selected from divalent organic groups having 1 to 60 carbon atoms, preferably, divalent

fluoroalkylene groups, divalent fluoroalkylene group having an ether bond, etc. These groups can impart various functions such as heat resistance, stain-proofing, non-tackiness, optical properties (e.g. low refractive index), chemical resistance, electrical insulation, etc. to the polymer.

Specific examples of the divalent fluoroalkylene group include $-(CF_2)_m-(CH_2)_n-$, $-[CF_2CF(CF_3)]_m-(CH_2)_n-$, $-(CF_2CH_2)_m-(CH_2)_n-$, and $-[CF_2C(CF_3)_2]_m-(CH_2)_n-$ wherein m is a number of 1 to 20, and n is a number of 0 to 10.

Specific examples of the divalent fluoroalkylene group having the ether bond include $-(CF_2CF_2O)_m-CF_2-$, $-(CF_2CF_2CF_2O)_m-CF_2CF_2-$, $-[CF(CF_3)\ CF_2O]_m-CF(CF_3)-$, and $-(CF_2O)_m-(CF_2)_k-$ wherein m and k are the same or different and a number of 1 to 20.

Besides the above fluoroalkylene groups and the like, the group A^1 in the formula (2) may be one of the following hydrocarbon groups having 1 to 20 carbons:

$-(CH_2)_m-$ wherein m is a number of 1 to 20, a cyclohexylene group, $-(Ph)_a-$ wherein Ph is a phenylene group and a is an integer of 1 to 3, $-(CH_2)_{m1}-(Ph)_a-(CH_2)_{m2}-$ in which Ph and a are the same as defined above, m1 is a number of 1 to 5 and m2 is a number of 0 to 5,

$$\begin{array}{l} (CH_2)_{m3}-H \\ \quad | \\ -(C)_m \\ \quad | \\ (CH_2)_{m4}-H \end{array}$$

wherein m is a number of 1 to 20, m3 is a number of 0 to 10 and m4 is a number of 1 to 10, and the like.

One particularly preferable example of the repeating unit of the formula (1) is a repeating unit of the formula:

$$-CH_2-CF-$$
$$\quad\quad|$$
$$CF_2O-(CF_2O)_x-(CF_2CF_2O)_y-(CX^1_2CF_2CF_2O)_z-(CFX^2CF_2O)_w-CFX^3-Y^2 \quad (3)$$

wherein X^1 is a hydrogen atom, a fluorine atom or a chlorine atom, X^2 is a hydrogen atom, a chlorine atom, a methyl group or a trifluoromethyl group, X^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, x, y, z and w are the same or different and a number of 0 to 20 provided that the sum of x, y, z and w is from 1 to 20, and Y^2 is -COOH, $-COOR^4$ in which R^4 is a hydrocarbon group having 1 to 20 carbon atoms, $-CH_2OH$, $-CON\langle^{R^5}_{R^6}$ in which R^5 and R^6 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, or $-OCO-CZ^6=CZ^4Z^5$ in which Z^4 and Z^5 are the same or different and a hydrogen atom or a fluorine atom, and Z^6 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group.

Preferable examples of the flurinated allyl ether (3) include $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COOCH_3$,

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)COOCH_3$,

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COOH$,

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)COOH$,

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CH_2OH$,

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)CH_2OH$, etc.

The preparation method of the fluorinated allyl ether (3) of the present invention will be explained. To simplify the formulas, "$-(CF_2O)_x-(CF_2CF_2O)_y-(CX^1_2CF_2CF_2O)_z-(CFX^2CF_2O)_w-CFX^3-$" will be represented by "Rf" in the following description.

The fluorinated allyl ether (3) of the present invention can be easily synthesized by defluoroiodination of a compound

having a terminal iodine atom of the formula:

$$ICH_2CF_2CF_2O\text{-}Rf\text{-}R \qquad (5).$$

The fluoroiodination is preferably carried out in a solvent (e.g. dimethylformamide, dimethylsulfoxide, methanol, acetone, methyl ethyl ketone, ethyl acetate, etc.) in the presence of a catalyst (e.g. zinc, copper, etc.) at a temperature of -20 to 200°C, preferably 50 to 150°C.

The polymer consisting of the chains of the repeating unit of the formula (1) of the present invention may be prepared as follows:

The homopolymerization of the fluorinated allyl ether (1) of the present invention is carried out by a conventional radial polymerization method under conventional radical polymerization conditions. Preferably, the radical polymerization using a radical initiating source (e.g. a radical polymerization initiator, light, heat, etc.) is used, and the polymerization mode may be bulk polymerization, solution polymerization, emulsion polymerization, suspension polymerization, etc.

The conditions employed in the radical polymerization are not limited and may include a temperature of 0 to 100°C and a pressure of atmospheric pressure, a reduced pressure down to about 760 mmHg or an elevated pressure up to about 100 kg/cm^2.

Alternatively, a functional group can be introduced in the polymer obtained by reacting the polymer with a compound having a functional group.

For example, when a polymer, which is obtained by polymerizing the fluorinated allyl ether (4) having the $-CH_2OH$ group, is reacted with a compound of the formula: $CZ^1Z^2{=}CZ^3COF$

wherein Z^1 and Z^2 are the same as defined above, a group of the formula: $-CH_2OCO-CZ^3=CZ^1Z^2$ can be introduced in the polymer.

Alternatively, when a polymer obtained by polymerizing the fluorinated allyl ether (4) having the $-OCF(CF_3)COOH$ group is treated with sodium hydroxide, etc. to change this group to an alkali salt and then heated to decarboxylate the polymer, the $-OCF=CF_2$ group can be introduced in the polymer.

The fluorinated allyl ether of the present invention can provide a high molecular weight product through the radical homopolymerization, and when the fluorinated allyl ether having the functional group is used, the polymer having the functional group in the molecule can be easily obtained. Such polymers have various properties depending on the functional groups contained therein, and they may be used as solvent-resistant polymers, water-soluble polymers, ion-exchange resins, reactive polymers, etc.

The present invention will be explained in detail by the following examples.

Example 1

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COOCH_3$ (5 g) and a 8 wt.% solution of $[H(CF_2CF_2)_3COO-]_2$ (hereinafter referred to as "DHP") in trichlorotrifuoroethane (0.5 g) were charged in a glass vessel. When the internal atmosphere in the vessel was replaced with nitrogen and the mixture was stirred at room temperature for 24 hour, the viscosity of the mixture increased. Low boiling materials were distilled off from the reaction mixture under reduced pressure to obtain a colorless transparent polymer (4.67 g).

When a molecular weight was calculated on the assumption that the initiator efficiency was 1 (one), no chain transfer reaction took place, and the termination was only rebonding termination, it was 71,652. Hereinafter, the molecular weight calculated as above will be referred to as a "calculated molecular weight".

The polymer obtained was soluble in tetrahydrofuran (THF). The polymer was dissolved in THF, and its molecular weight was measured with GPC using polystyrene as a standard. A number average molecular weight was about 68,000. This number average molecular weight measured with GPC was in good agreement with the calculated molecular weight. Thus, in the following Examples, only calculated molecular weights are reported.

The polymer had Tg of -2°C and a refractive index of 1.3132.

Herein, Tg was measured with DSC (differential scanning calorimeter), and a refractive index was measured with an Abbe refractometer.

Example 2

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)CH_2OH$ was polymerized in the same manner as in Example 1, and a colorless transparent polymer (2.10 g) was obtained. It had a calculated molecular weight of 32,865, Tg of -4°C and a refractive index of 1.3416.

Example 3

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COOH$ was polymerized in the same manner as in Example 1, and a white polymer (4.77 g) was obtained. It had a calculated molecular weight of 74,651 and Tg of 13°C. This polymer was soluble in water, and pH of the aqueous solution (concentration: 1 wt. %) was about 2. The aqueous solution was

foamable.

Example 4

Polymerization was carried out in the same manner as in Example 1 except that $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CH_2OH$ (5.0 g) and DHP (0.51 g) were used, and a colorless transparent polymer (4.68 g) was obtained. This polymer was a hard solid at room temperature, and it had a calculated molecular weight of 80,730.

Example 5

Polymerization was carried out in the same manner as in Example 1 except that $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)COOCH_3$ (5.01 g) and DHP (0.53 g) were used, and a colorless transparent polymer (4.54 g) was obtained. This polymer was soft at room temperature, and it had a calculated molecular weight of 73,880.

Example 6

$CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)CH_2OH$ (Monomer A) (14. g), $CH_2=CFCF_2OCF(CF_3)CF_2OCF(CF_3)COOCH_3$ (Monomer B) (6 g) and DHP (8.29 g; 8 wt. % solution in perfluorohexane) were mixed with HCFC-225 (a mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane) (5 g), and the mixture was stirred at 30°C for 24 hours.

The resulting solution was poured in petroleum benzine to precipitate the polymer formed.

The polymer precipitated was recovered, washed with petroleum benzine, and dried under reduced pressure to obtain a rubbery polymer (18 g).

According to NMR analysis, the polymer obtained was a copolymer containing Monomer A and Monomer B in a molar ratio of 81:19.

Example 7

The fluorine-containing copolymer obtained in Example 6 (13 g) was dissolved in HCFC-225 (30 g), and the pyridine (0.61 g) was added to the solution, followed by cooling to 0 to 5°C. Then, CH_2=CFCOF (3.0 g) was gradually dropwise added to the solution while cooling with ice and stirring, and then the solution was stirred for additional 4 hours.

The polymer was precipitated washed and dried in the same manner as in Example 6 to obtain a rubbery polymer (10 g).

In the NMR chart of the obtained polymer, the absorption assigned to the OH groups disappeared, while the absorption assigned to >C=C< appeared.

According to NMR analysis, in the polymer obtained, the molar ratio of the monomer having $-COOCH_3$ to the monomer having $-OCO-CF=CH_2$ was 80:20.

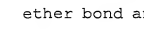
CLAIMS

1. (Amended) A fluorine-containing allyl ether polymer having a number average molecular weight of 1,000 to 1,000,000 and consisting of chains of at least one repeating unit selected from the group consisting essentially of a repeating unit of the formula:

(1)

wherein A is alkyl or fluoroalkyl groups having 1 to 50 carbon atoms, alkenyl or fluoroalkenyl groups having 2 to 50 carbon atoms, alkynyl or fluoroalkynyl groups having 2 to 50 carbon atoms, alkyl or fluoroalkyl groups having an ether bond and 1 to 60 carbon atoms, alkenyl or fluoroalkenyl groups having an ether bond and 2 to 60 carbon atoms, alkynyl or fluoroalkynyl groups having an ether bond and 2 to 60 carbon atoms, aryl or fluoroaryl groups having 4 to 30 carbon atoms,

and a repeating unit of the formula:



(2)

wherein A^1 is a divalent organic group having 1 to 60 carbon atoms, and Y^1 is $-CH_2OH$, $-COOH$, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CON<^{R^2}_{R^3}$ in which R^2 and R^3 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, or $-OCO-CZ^3=CZ^1Z^2$ in which Z^1 and Z^2 are the same or different and a hydrogen atom or a fluorine atom, and Z^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group.

2. (Cancelled)

3. (Amended) The fluorine-containing allyl ether polymer according to claim 1 or 7, wherein A^1 in the formula (2) is a fluoroalkylene group having 1 to 60 carbon atoms or a fluoroalkylene group having an ether bond and 1 to 60 carbon atoms.

4. (Amended) The fluorine-containing allyl ether polymer according to claim 1, 3 or 7, wherein at least one of the repeating units is a repeating unit of the formula:

$$-CH_2-CF(-CF_2O-(CF_2O)_x-(CF_2CF_2O)_y-(CX^1{}_2CF_2CF_2O)_z-(CFX^2CF_2O)_w-CFX^3-Y^2)- \quad (3)$$

wherein X^1 is a hydrogen atom, a fluorine atom or a chlorine atom, X^2 is a hydrogen atom, a chlorine atom, a methyl group or a trifluoromethyl group, X^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, x, y, z and w are the same or different and a number of 0 to 20 provided that the sum of x, y, z and w is from 1 to 20, and Y^2 is -COOH, $-COOR^4$ in which R^4 is a hydrocarbon group having 1 to 20 carbon atoms, $-CH_2OH$, $-CON{<}^{R^5}_{R^6}$ in which R^5 and R^6 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, or $-OCO-CZ^6=CZ^4Z^5$ in which Z^4 and Z^5 are the same or different and a hydrogen atom or a fluorine atom, and Z^6 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group.

5. A fluorine-containing allyl ether polymer represented by the formula:

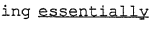
$$CH_2=CFCF_2O-(CF_2O)_x-(CF_2CF_2O)_y-(CX^1{}_2CF_2CF_2O)_z-(CFX^2CF_2O)_w-CFX^3-R \quad (4)$$

wherein X^1 is a hydrogen atom, a fluorine atom or a chlorine atom, X^2 is a hydrogen atom, a chlorine atom, a methyl group or a trifluoromethyl group, X^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, x, y, z and w are the same or different and a number of 0 to 20 provided that the sum of x, y, z and w is from 1 to 20, and R is -COOH, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CH_2OH$, $-CONH_2$, $-CF=CF_2$, a hydrocarbon group having 1 to 20 carbon atoms or a perfluoroalkyl group having 1 to 20 carbon atoms.

6. The fluorine-containing allyl ether polymer according

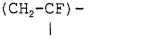
to claim 5, which has a number average molecular weight of 1,000 to 1,000,000.

7. (Amended) A fluorine-containing allyl ether copolymer consisting essentially of chains of at least two repeating units of the formula:



(5)

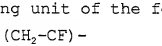
wherein A^2 is an organic group having 1 to 100, wherein at least one repeating unit is ~~selected from the group consisting of~~ a repeating unit of the formula:



(1)

wherein A is alkyl or fluoroalkyl groups having 1 to 50 carbon atoms, alkenyl or fluoroalkenyl groups having 2 to 50 carbon atoms, alkynyl or fluoroalkynyl groups having 2 to 50 carbon atoms, alkyl or fluoroalkyl groups having an ether bond and 1 to 60 carbon atoms, alkenyl or fluoroalkenyl groups having an ether bond and 2 to 60 carbon atoms, alkynyl or fluoroalkynyl groups having an ether bond and 2 to 60 carbon atoms, aryl or fluoroaryl groups having 4 to 30 carbon atoms,

and at least one repeating unit is a repeating unit of the formula:



(2a)

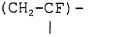
wherein A^1 is a divalent organic group having 1 to 60 carbon atoms, and Y^1 is $-CH_2OH$, $-COOH$, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CON<^{R^2}_{R^3}$ in which R^2 and R^3 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, $-OCO-CZ^3=CZ^1Z^2$ in which

Z^1 and Z^2 are the same or different and a hydrogen atom or a fluorine atom, and Z^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, an epoxy group, a glycidyl group, a cyano group, a sulfonic acid group or a $-SO_3R'$ in which R' is a monovalent organic group.

8. (Cancelled)

CLAIMS

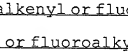
1. (Amended) A fluorine-containing allyl ether polymer having a number average molecular weight of 1,000 to 1,000,000 and consisting of chains of at least one repeating unit selected from the group consisting of a repeating unit of the formula:



(1)

wherein A is alkyl or fluoroalkyl groups having 1 to 50 carbon atoms, alkenyl or fluoroalkenyl groups having 2 to 50 carbon atoms, alkynyl or fluoroalkynyl groups having 2 to 50 carbon atoms, alkyl or fluoroalkyl groups having an ether bond and 1 to 60 carbon atoms, alkenyl or fluoroalkenyl groups having an ether bond and 2 to 60 carbon atoms, alkynyl or fluoroalkynyl groups having an ether bond and 2 to 60 carbon atoms or aryl or fluoroaryl groups having 4 to 30 carbon atoms,

and a repeating unit of the formula:



(2)

wherein A^1 is a divalent organic group having 1 to 60 carbon atoms, and Y^1 is $-CH_2OH$, $-COOH$, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CON<\frac{R^2}{R^3}$ in which R^2 and R^3 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, or $-OCO-CZ^3=CZ^1Z^2$ in which Z^1 and Z^2 are the same or different and a hydrogen atom or a fluorine atom, and Z^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group.

2. (Cancelled)

3. (Amended) The fluorine-containing allyl ether polymer

according to claim 1, 7 or 8, wherein A^1 in the formula (2) is a fluoroalkylene group having 1 to 60 carbon atoms or a fluoroalkylene group having an ether bond and 1 to 60 carbon atoms.

4. (Amended) The fluorine-containing allyl ether polymer according to claim 1, 3, 7 or 8, wherein at least one of the repeating units is a repeating unit of the formula:

$$-CH_2-CF-$$
$$|$$
$$CF_2O-(CF_2O)_x-(CF_2CF_2O)_y-(CX^1{}_2CF_2CF_2O)_z-(CFX^2CF_2O)_w-CFX^3-Y^2 \quad (3)$$

wherein X^1 is a hydrogen atom, a fluorine atom or a chlorine atom, X^2 is a hydrogen atom, a chlorine atom, a methyl group or a trifluoromethyl group, X^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, x, y, z and w are the same or different and a number of 0 to 20 provided that the sum of x, y, z and w is from 1 to 20, and Y^2 is -COOH, $-COOR^4$ in which R^4 is a hydrocarbon group having 1 to 20 carbon atoms, $-CH_2OH$, $-CON<^{R^5}_{R^6}$ in which R^5 and R^6 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, or $-OCO-CZ^6=CZ^4Z^5$ in which Z^4 and Z^5 are the same or different and a hydrogen atom or a fluorine atom, and Z^6 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group.

5. A fluorine-containing allyl ether polymer represented by the formula:

$$CH_2=CFCF_2O-(CF_2O)_x-(CF_2CF_2O)_y-(CX^1{}_2CF_2CF_2O)_z-(CFX^2CF_2O)_w-CFX^3-R \quad (4)$$

wherein X^1 is a hydrogen atom, a fluorine atom or a chlorine atom, X^2 is a hydrogen atom, a chlorine atom, a methyl group or a trifluoromethyl group, X^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, x, y, z and w are the same or different and a number of 0 to 20 provided that the sum of x, y, z and w is from 1 to 20, and R is -COOH, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CH_2OH$, $-CONH_2$, $-CF=CF_2$, a hydrocarbon group having 1 to 20 carbon atoms or a perfluoroalkyl group having 1 to 20 carbon atoms.

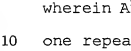
6. The fluorine-containing allyl ether polymer according

to claim 5, which has a number average molecular weight of 1,000 to 1,000,000.

7. (New) A fluorine-containing allyl ether copolymer consisting of chains of at least two repeating units of the formula:

(5)

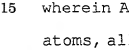
wherein A^2 is an organic group having 1 to 100, wherein at least one repeating unit is selected from the group consisting of a repeating unit of the formula:



(1)

wherein A is alkyl or fluoroalkyl groups having 1 to 50 carbon atoms, alkenyl or fluoroalkenyl groups having 2 to 50 carbon atoms, alkynyl or fluoroalkynyl groups having 2 to 50 carbon atoms, alkyl or fluoroalkyl groups having an ether bond and 1 to 60 carbon atoms, alkenyl or fluoroalkenyl groups having an ether bond and 2 to 60 carbon atoms, alkynyl or fluoroalkynyl groups having an ether bond and 2 to 60 carbon atoms or aryl or fluoroaryl groups having 4 to 30 carbon atoms,

and a repeating unit of the formula:



(2a)

wherein A^1 is a divalent organic group having 1 to 60 carbon atoms, and Y^1 is $-CH_2OH$, $-COOH$, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CON<_{R^3}^{R^2}$ in which R^2 and R^3 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, $-OCO-CZ^3=CZ^1Z^2$ in which

Z^1 and Z^2 are the same or different and a hydrogen atom or a fluorine atom, and Z^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, an epoxy group, a glycidyl group, a cyano group, a sulfonic acid group or a $-SO_3R'$ in which R' is a monovalent organic group.

8. (New) The fluorine-containing allyl ether copolymer according to claim 7, wherein at least one repeating unit is a repeating unit of the formula:

$$-(CH_2-CF)-$$
$$\quad\quad|$$
$$CF_2-O-A^1-Y^1 \qquad (2a)$$

wherein A^1 is a divalent organic group having 1 to 60 carbon atoms, and Y^1 is $-CH_2OH$, $-COOH$, $-COOR^1$ in which R^1 is a hydrocarbon group having 1 to 20 carbon atoms, $-CON<^{R^2}_{R^3}$ in which R^2 and R^3 are the same or different and a hydrogen atom or a hydrocarbon group having 1 to 20 carbon atoms, $-O-CF=CF_2$, $-OCO-CZ^3=CZ^1Z^2$ in which Z^1 and Z^2 are the same or different and a hydrogen atom or a fluorine atom, and Z^3 is a hydrogen atom, a fluorine atom, a chlorine atom or a trifluoromethyl group, an epoxy group, a glycidyl group, a cyano group, a sulfonic acid group or a $-SO_3R'$ in which R' is a monovalent organic group.

Attorney Docket No.
0020-4902P

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PLEASE NOTE:
YOU MUST
COMPLETE THE
FOLLOWING

COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT AND DESIGN APPLICATIONS

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title:

FLUORINATED ALLYL ETHER POLYMER

Fill in Appropriate Information - For Use Without Specification Attached:

the specification of which is attached hereto. If not attached hereto,
the specification was filed on _____ as
United States Application Number _____ ;
and amended on _____ (if applicable) and/or
the specification was filed on March 10, 2000 as PCT
International Application Number PCT/JP00/01453 ; and was
amended under PCT Article 19 on February 6, 2001 and April 27, 2001 (if applicable)
34

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representative or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Insert Priority Information: (if appropriate)

Prior Foreign Application(s)			Priority Claimed	
64577/1999 (Number)	Japan (Country)	3/11/1999 (Month/Day/Year Filed)	☑ Yes	☐ No
(Number)	(Country)	(Month/Day/Year Filed)	☐ Yes	☐ No
(Number)	(Country)	(Month/Day/Year Filed)	☐ Yes	☐ No
(Number)	(Country)	(Month/Day/Year Filed)	☐ Yes	☐ No

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional applications(s) listed below.

Insert Provisional Application(s): (if any)

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More than 12 Months (6 Months for Designs) Prior to the Filing Date of This Application:

Insert Requested Information: (if appropriate)

Country	Application Number	Date of Filing (Month/Day/Year)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States and/or PCT application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States and/or PCT application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to the patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

Insert Prior U.S. Application(s): (if any)

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)
(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)

0020-4902P

Attorney Docket No.

I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

Raymond C. Stewart	(Reg. No. 21,066)	Terrell C. Birch	(Reg. No. 19,382)
Joseph A. Kolasch	(Reg. No. 22,463)	James M. Slattery	(Reg. No. 28,380)
Bernard L. Sweeney	(Reg. No. 24,448)	Michael K. Mutter	(Reg. No. 29,680)
Charles Gorenstein	(Reg. No. 29,271)	Gerald M. Murphy, Jr.	(Reg. No. 28,977)
Leonard R. Svensson	(Reg. No. 30,330)	Terry L. Clark	(Reg. No. 32,644)
Andrew D. Meikle	(Reg. No. 32,868)	Marc S. Weiner	(Reg. No. 32,181)
Joe McKinney Muncy	(Reg. No. 32,334)	Donald J. Daley	(Reg. No. 34,313)
John W. Bailey	(Reg. No. 32,881)	John A. Castellano	(Reg. No. 35,094)
Gary D. Yacura	(Reg. No. 35,416)		

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PLEASE NOTE: YOU MUST COMPLETE THE FOLLOWING:

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of First Joint Inventor: Insert Name of Inventor → Insert Date This Document is Signed

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
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MAILING ADDRESS (Complete Street Address including City, State & Country)		
c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		

Insert Residence
Insert Citizenship →
Insert Post Office Address →

Full Name of Second Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Hirotoshi SAKASHITA	Hirotoshi Sakashita	August 10, 2001
Residence (City, State & Country)		CITIZENSHIP
Settsu-shi, Osaka, Japan JPX		Japan
MAILING ADDRESS (Complete Street Address including City, State & Country)		
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Full Name of Third Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
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Residence (City, State & Country)		CITIZENSHIP
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MAILING ADDRESS (Complete Street Address including City, State & Country)		
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Full Name of Fourth Inventor, if any: see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Tetsuo SHIMIZU	Tetsuo Shimizu	August 22, 2001
Residence (City, State & Country)		CITIZENSHIP
Settsu-shi, Osaka, Japan JPX		Japan
MAILING ADDRESS (Complete Street Address including City, State & Country)		
c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		

*DATE OF SIGNATURE